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Characterization of Plasma Polymerized Hydrocarbons
Using CP-MAS Carbon-13 NMR

by

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Synopsis

Plasma polymerized hydrocarbons made from ethane and methane were produced under different reactor conditions and probed by solid-state carbon-13 nuclear magnetic resonance (NMR) with cross-polarization and magic angle sample spinning. NMR experiments provided structural information about the plasma polymers. The conditions of low power, high hydrocarbon gas flow rate, and no added hydrogen gas appeared to give the highest amount of non-protonated sp^3 hybridized carbons in the films for the reactor design used. The use of methane or ethane as reactor gas did not affect plasma polymer structure significantly.

Introduction

Plasma polymerized thin films are of interest because of their potential end use.^{1,2} Small amounts of these materials deposited on a substrate can enhance surface properties such as chemical inertness, permeability, biocompatibility, hydrophilicity, adhesion, and conductivity without effecting the properties of the bulk substrate. Variations in the reactor parameters can produce significantly different plasma polymers with different chemical properties from the same monomer. However, little is known about the chemical structure of plasma polymerized materials as a function of critical reactor parameters.

The intractability of plasma polymers precludes the use of many analytical techniques for structural determination. The most widely used spectroscopic tools for analyzing these materials is Fourier transform infrared spectroscopy (FTIR)¹⁻⁴ and electron spectroscopy for chemical analysis (ESCA).^{1-3,5} Although both techniques are of utility, they have significant limitations. FTIR readily provides functional group information, but it is limited due to the difficulty in obtaining extinction coefficients for various functional groups associated with an array of environments. ESCA provides excellent structural information in fluorinated plasma polymers, but the small differences in C_{1s} core level binding energies in hydrocarbon structures makes interpretation difficult.^{1-3,5,6}

Cross-polarization (CP), magic angle spinning (MAS) carbon-13 NMR studies are a potential source for complimentary structural information. Despite the need for structural information in the plasma polymer field, there are only a few reports of the application of CP-MAS NMR on plasma polymers. This is probably because the amount of sample required for NMR analysis is large. Kaplan *et al.*^{5,7-9} have conducted studies of plasma polymers produced from hydrocarbon gases using CP-MAS NMR. The effects of using ethane, ethylene, acetylene, and toluene as the monomer under the same reactor conditions on plasma polymer structure were reported. The advantages of carbon-13 labeling of the monomer in terms of increased sensitivity for functional groups and mechanistic information, were also demonstrated using CP-MAS NMR.⁹ In addition a

comparison of the various spectroscopic techniques currently used for plasma polymer analysis was made.⁵

Recently, thin films which possess the diamond structure have become the goal of many in the plasma polymerization field for an array of applications.¹⁰ In this paper, we report the use of carbon-13 CP-MAS NMR¹¹ to study the effects of plasma polymerization reactor parameters on the plasma polymer structure and, within this limited study, evaluate conditions for producing material with the highest content of non-protonated sp^3 hybridized carbons.

Experimental

A bell-jar type reactor described previously was used for plasma polymerization.¹² The reactor utilizes a pair of magnetically enhanced electrodes (planar magnetrons) driven by 10 kHz alternating electric current. Slide glass plates (for a microscope) were mounted, by means of mechanical clamps, on both sides of an aluminum plate (14 in. diameter) which was placed in the mid-point of two electrodes and rotated by a motor at a constant speed (50 rpm) along the axis placed above the two electrodes. Each glass plate travels parallel to the electrode surface and in-through-out of the plasma zone which is created between two electrodes.

The conditions for plasma polymerization are given in Table I. The flow rate of a gas was controlled by a Tylan mass flow controller which was calibrated for each gas. Plasma polymerization under a given set of conditions was carried out for a long period of time (e.g. a few hours) in order to accumulate enough deposited material. The sample was collected by scraping off the polymer deposited on the glass plates. Plasma polymerization was repeated until enough sample was collected for NMR measurement (approximately 150 mg). Product was then packed into NMR MAS spinners. During packing and analysis, the polymers came in contact with atmospheric oxygen.

Carbon-13 NMR spectra were collected on a Varian VXR-200 with a Larmor frequency of 50 MHz. The cross-polarization pulse sequence was used with high power decoupling and magic angle spinning on all samples. The cross-polarization pulse sequence was repeated for 50 000 to 100 000 scans for each sample with a 1.0 second pulse delay. This corresponded to an experiment duration of 12-24 hours (larger sample amounts would reduce this time significantly). Contact times were typically 1.0 ms. The magic angle spinning rates were between 3.5 to 4.8 kHz. In addition to the standard cross polarization pulse sequence, proton dephased (PDP) spectra were collected to enhance the non-protonated carbon spectra.¹³ The delay used for proton dephasing was 40-75 μ s. Spectra were externally referenced to hexamethylbenzene but reported relative to tetramethylsilane.

Results and Discussion

The carbon-13 CP-MAS spectra of the plasma polymers produced under the conditions in Table I are shown in Figure 1. These spectra were collected with the standard cross-polarization pulse sequence, therefore, all carbon environments which cross-polarize are represented in these spectra. The carbon-13 chemical shifts for sp^2 hybridized carbons are typically 100-150 ppm and the range for sp^3 hybridized carbons is between 10 and 60 ppm. The ratio of sp^2 to sp^3 carbon intensities for the spectra in Figure 1 are shown in Table II. The CP-MAS PDP spectra shown in Figure 2 are representative of those without strong dipolar coupling. This includes non-protonated carbons and carbons with highly mobile hydrogens such as methyl groups.

The intensities in the spectra are assumed to be representative of the various types of carbons present. Generally, there are several sources for error in treating carbon-13 CP-MAS data quantitatively. Intensity distortions could be due to spinning side bands, differential cross polarization times for carbons in different environments and different spin-lattice relaxation times in the rotating frame. Because of the limited amounts of samples available, the details of these processes have not been studied for these samples. It is assumed that the highly disordered structure of the plasma polymers enables effective cross-polarization of all carbon-13 nuclei with nearby protons. If large domains of proton poor species existed, they would be underrepresented in the spectra

The most prominent characteristic of the spectra in Figure 1 is the breadth of the resonances. The broad line shapes are due to the distribution of carbon environments produced in the plasma polymerization process and not the natural line widths of individual species. The plasma polymerization of the sp^3 hybridized monomers produced products with varying degrees of sp^2 and sp^3 nature. The contributions of sp^3 and sp^2 hybridized carbons are well resolved because the chemical shift ranges do not overlap. Further structural distinctions can be made based on chemical shifts. Methyl groups usually have chemical shifts in the range of 10-30 ppm. Methylenes and methines have chemical shifts in the range of 20-60 ppm and quaternary carbons

usually lie in the range of 30-55 ppm. The overlap of these types of sp^3 carbons makes spectral interpretation difficult in the case of plasma polymers.

The CP-MAS NMR spectra of samples B, C and D contain the same general features as those of A, despite the different reactant gases that were used in C and D. Hydrogen gas was also used in C. Although the signal to noise ratio in the sample D spectrum is poor (because of very low sample amount) the resonance positions and intensities in this spectrum, when compared to those of sample C, suggest that hydrogen does not significantly affect plasma polymer structure at high values of the power to flow-rate ratio (W/F). This was previously noted for fluorocarbons.¹⁴ The ratio of the peak areas of sp^2 and sp^3 regions of samples C and D are also similar. The fact that the spectral features of sample B are similar to C and D indicates the choice of ethane or methane as reactant gas does not significantly affect plasma polymer structure under high W/F.

The minimum amount of intensity in the carbonyl region (155-220 ppm) of all spectra indicates these groups are not present in large amounts, however, sensitivity to carbonyls groups may be low because of the cross-polarization pulse sequence. The small amount of intensity in this region is primarily due to spinning side bands. Therefore, atmospheric oxygen did not react to any great extent with residual free radicals on the plasma polymer surface upon exposure.

The relative amounts of non-protonated sp^2 and non-protonated sp^3 structures may be determined by inserting a delay without dipolar decoupling before data acquisition. The symbolic structures for these carbons found in the PDP spectra are shown below.



During the delay for PDP spectra, protonated carbons which are relatively immobile are dephased due to dipole-dipole interactions. Protonated nuclei are strongly effected by the interactions with protons because the strength of the interaction is a function of internuclear distance (proportional to $1/r^3$). The interaction drops off too rapidly to effect non-protonated carbons to the same extent as protonated carbons. For methyl groups, the C-H bond vector reorients rapidly and reduces the

strength of the interaction. Generally, liquid samples are not affected by static dipole-dipole interactions because they are averaged by molecular motion. The proton dephased spectra are primarily representative of non-protonated carbons and mobile species. The relative amounts of non-protonated sp^2 and sp^3 carbons may be estimated using PDP spectra because they are each in a distinct chemical shift range and the quaternary carbon intensity can be separated from the methyl group intensity.

Close inspection of the sample A CP-MAS spectrum relative to the other samples reveals methyl group resonances are more noticeable in the 10-30 PPM region. These resonances are more pronounced in the CP-MAS PDP spectra because immobile methylene and methine carbon intensity is diminished. The split resonance in the methyl region of the sample A PDP spectrum is a function of the hybridization of the adjacent carbon and the degree of branching from the attached carbon. If the adjacent carbon is sp^2 hybridized *cis* or *trans* configurations will also play a role in chemical shift.¹⁵ In the PDP spectra of samples B and C there is very little methyl group intensity and it is concluded that methyl groups are not very abundant. The PDP spectra also reveal that the sample A conditions produces more non-protonated sp^3 than non-protonated sp^2 carbons. Although there is little non-protonated sp^3 or methyl group intensity in samples B and C spectra there is considerable non-protonated sp^2 carbon intensities.

Comparison of the spectra of the samples in this paper with those of Kaplan, Dilks and Van Laeken reveals that plasma polymers are highly sensitive to the reactor conditions.^{5,7,8} Sample A which has the reactor conditions closest to those used in the Dilks *et al.* study has similar structural features to their ethane and ethylene plasma polymers. Although the reactor design and sample positioning may also have an effect on plasma polymer structure, relatively low power and high reacting gas flow rates tend to produce plasma polymers with more sp^3 character and more methyl groups. The samples prepared under harsher conditions, high power and low reactive gas flow rates, had more sp^2 character and minimal methyl group content.

The separation between sp^2 and sp^3 hybridized carbons in the NMR spectra is far superior to that obtained from ESCA. Further distinctions can be made on the basis of chemical shift for

methyl, methylene and methine resonance positions. The identification of the relative amount of non-protonated sp^3 carbons is important because their chemical resistivity may be a desirable property in many plasma coatings applications. Therefore, determination of the reactor parameters which produce these materials is an important step in optimizing these properties.

Conclusions

Solids CP-MAS DD ^{13}C NMR is a valuable tool for the elucidation of chemical structures of plasma polymerized hydrocarbons. High monomer flow rates with low power tend to produce plasma polymers with more sp^3 character. The substitution of methane for ethane as monomer gas does not appear to effect plasma polymer structure to a significant extent. The presence of hydrogen gas does not effect the sp^2/sp^3 ratio.

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Table I
Polymerization Conditions

Sample	Hydrocarbon Gas	Flow Rate	Power	H ₂ Flow Rate
A	CH ₃ -CH ₃	10.0 cc/min	45 watts	-----
B	CH ₃ -CH ₃	1.0 cc/min	100 watts	-----
C	CH ₄	0.5 cc/min	112.5 watts	1.0 cc/min
D	CH ₄	1.0 cc/min	150 watts	-----
E*	CH ₃ -CH ₃	4.0 cc/min	10 watts	-----
F*	CH ₂ =CH ₂	4.0 cc/min	10 watts	-----
G*	CH≡CH	4.0 cc/min	10 watts	-----

*Reference 7

Table II
Relative Peak Areas

Sample	sp ²	sp ³	sp ² /sp ³
A	0.17	0.83	0.20
B	0.48	0.52	0.92
C	0.39	0.61	0.64
D	0.39	0.61	0.64
E*	0.19	0.81	0.23
F*	0.24	0.76	0.32
G*	0.38	0.62	0.61

*Reference 7

Figure Captions

Figure 1. Carbon-13 CP/MAS spectra for plasma polymers from ethane (A, B) and methane (C, D). See Table I for reaction conditions.

Figure 2. Carbon-13 CP/MAS spectra for plasma polymers from ethane (A, B) and methane (C) with proton dephasing (PDP). See Table I for reaction conditions.

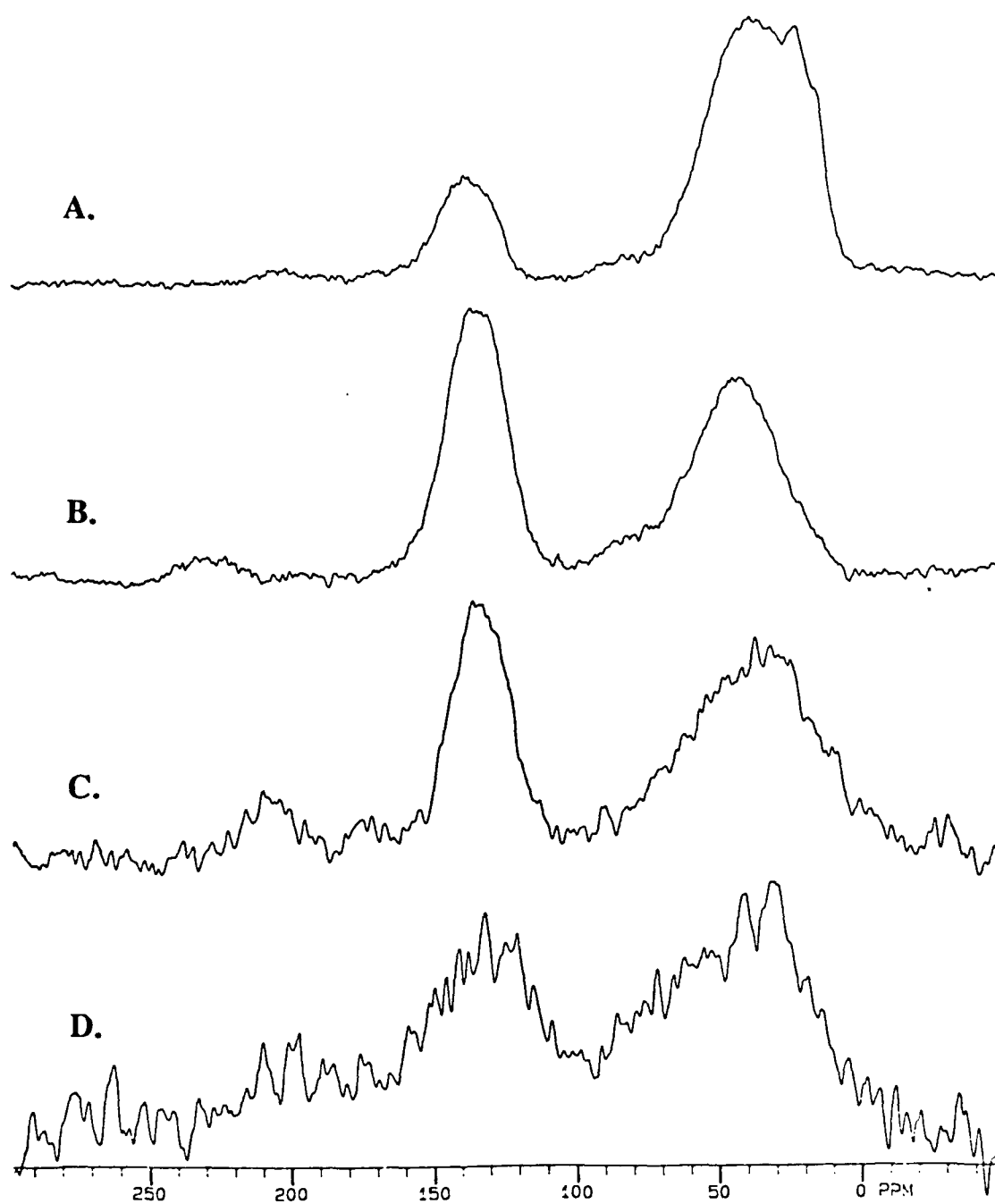


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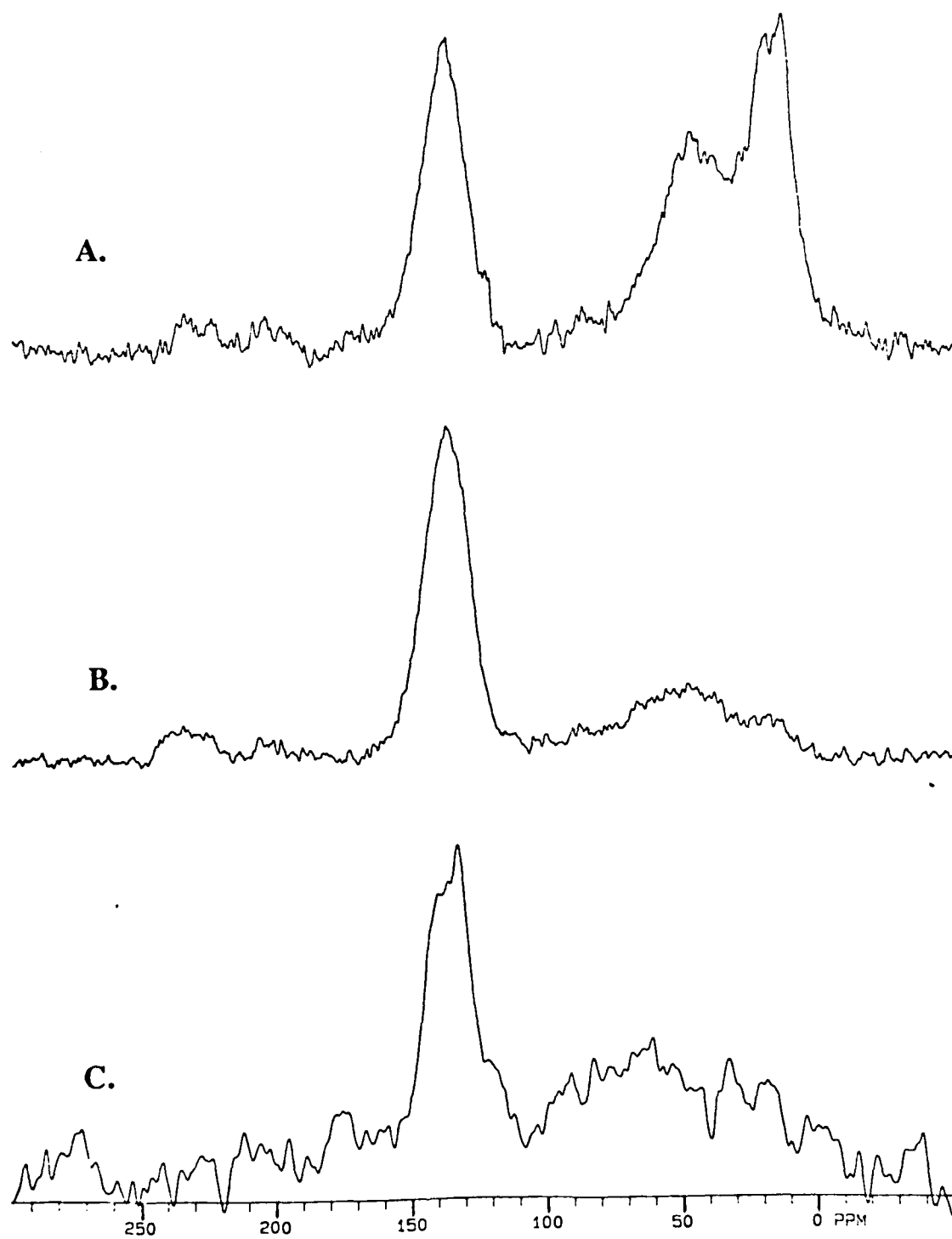


Figure 2. Carbon-13 CP/MAS spectra for plasma polymers from ethane (A, B) and methane (C) with proton dephasing (PDP). See Table I for reaction conditions.